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Seasonal Influence on Vapor- and Particle-Phase Polycyclic Aromatic Hydrocarbon Concentrations in School Communities Located in Southern California

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Ambient concentrations of 15 vapor- and particle-phase (PM$_{2.5}$) polycyclic aromatic hydrocarbons (PAHs), listed by the US EPA as priority pollutants, were measured between July 2002 and November 2003 in six Southern California communities participating in a multi-year chronic respiratory health study of schoolchildren. The communities were geographically distributed over two hundred kilometers, extending from Long Beach in coastal Los Angeles, to high mountain areas to the north and west of the Los Angeles basin, and south into Eastern San Diego County. Seasonal and spatial variation in the atmospheric concentrations of PAHs is of interest because this class of compounds includes potent mutagens, carcinogens, and species capable of generating reactive oxygen species (ROS) that may lead to oxidative stress. Naphthalene accounted for 95% of the total PAH mass; annual averages ranged from 89 to 142 ng m^{-3}. Benzo[*ghi*]perylene (BGP) and the pro-carcinogen benzo[*a*]pyrene (BAP), present almost exclusively in the particle-phase, ranged respectively from 38 to 231 pg m^{-3} and 75 and 111 pg m^{-3}, with the highest values observed in Long Beach, a community with a high volume of seaport-related activities, and Lancaster, a commuter dormitory community. A considerable increase in the particle-phase PAH concentration, relative to the vapor-phase, was observed as ambient temperature decreased. Cold/hot season ratios for PAHs in PM$_{2.5}$ averaged 5.7, reaching 54 at Long Beach.

The presented data underscore the importance of seasonal variations on atmospheric PAH concentrations. These observations are relevant to future interpretation and analysis of community-scale human health effects research.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have been the focus of considerable mutagenicity and carcinogenicity research over several decades. In addition to their association with lung and other cancers (Saladi et al. 2003; Tchou-Wong et al. 2002), and adverse reproductive outcomes (Raychoudhury and Kubinski 2003; Sram et al. 1999), PAHs can also trigger acute respiratory responses such as asthma (Bommel et al. 2003; Delfino 2002). Recent studies have shown that PAHs associated with particulate matter (PM) are capable of generating reactive oxygen species (ROS), which have been linked to inflammatory responses of the human respiratory system (Cho et al. 2005; Li et al. 2004; Li et al. 2003). There is ample literature showing that PM is toxic to humans (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans 1989; Peng et al. 2005). More recently, a direct link between the PAH content of atmospheric PM and adverse health effects has been established (Pedersen et al. 2004; Xia et al. 2004).

PAHs are emitted or derived from a number of sources (Kleeman et al. 2000; Mastral and Callen 2000; Schauer et al. 2001). In Southern California, major sources of PAHs include engine exhaust emissions (diesel and gasoline), aircraft and ship emissions, combustion of oil and gas for power generation, wood burning in forest fires and residential fireplaces, and certain industrial sources. The 15 million registered on-road vehicles in the greater Los Angeles Basin are among the largest contributors to fresh emissions of both particle- and vapor-phase PAHs. The atmospheric concentrations of PAHs are governed by their source strength, and their chemical and physical stability while airborne. Once airborne, the major parameters thought to control the concentration of the aerosol containing PAHs include

their chemical reactivity, subcooled liquid vapor pressure and temperature-dependent phase-partitioning and atmospheric dilution. The results of our previous study carried out in 2001 and 2002 in four urban school communities located directly downwind of Central Los Angeles and two communities located in rural areas revealed that PAH concentrations in the urban communities are strongly impacted by atmospheric transport (Eiguren-Fernandez et al. 2004).

In the present one-year study, an attempt was made to gain an increased understanding of the role of season and atmospheric transport on the processes that affect PAH concentration in school communities geographically distributed over two hundred kilometers in Southern California.

2. EXPERIMENTAL

2.1. Sampling Sites

Ambient air sampling was performed at public school locations in six communities participating in a multi-year chronic respiratory health study of Southern California schoolchildren (Peters et al. 1999). Communities were selected for health study participation on the basis of historical air quality data, comparable population demographics, a sufficient number of potential subjects attending public school, available study funding, and the willingness of the local school district to participate (Figure 1). Sampling was carried out between 2002 and 2003 in Santa Maria, Lake Arrowhead, Lake Elsinore, Alpine, Long Beach, and Lancaster. Sampling was performed in three communities at a time over consecutive two-month periods. Samplers were relocated to the other three study communities after each two-month period, and the sampling protocol was repeated over an entire

year to obtain three sets of alternating seasonal measurements in each of the six communities. The six communities in the present study were geographically distributed over two hundred kilometers, extending from coastal Central California through coastal Los Angeles to high mountain areas located to the west in Riverside and San Bernardino counties, and south into Eastern San Diego County.

2.2. Sample Collection

Commercially available Semi-Volatile Organic Compound (SVOC) and $PM_{2.5}$ two-channel low volume air samplers (Tisch Environmental Model 1202, Cleves, OH) were deployed to community schools for sampling. Specific sampling locations varied between communities, but sampling sites shared several common characteristics: open, unobstructed sampling at a height of approximately five meters above ground. Specific sampler characteristics have been previously detailed (Eiguren-Fernandez et al. 2004). Briefly, particle- (PP) and vapor-phase (VP) samples were collected for 24 hr, every eighth day, at 113 lpm (mass flow meter controlled). Sampling periods of a few hours would have been preferable. However, the sampling locations were too far from each other to allow shorter sampling intervals. For all samplers and sites, final air sample volumes refer to $21.1°C$ and 101.3 kPa (according to US EPA protocol). A sampling matrix which comprised XAD-4 resin and quartz fiber filters (QFFs) was used to collect vapor- and particle-phase PAHs, respectively. We found that two layers of 10g of XAD-4 resin each yielded a collection efficiency of $\sim99\%$ for the target VP-PAHs. For this reason collection of vapor-phase PAHs was carried out using 20 g of XAD-4 (Acros Oganics, NJ) resin held in a glass cylinder
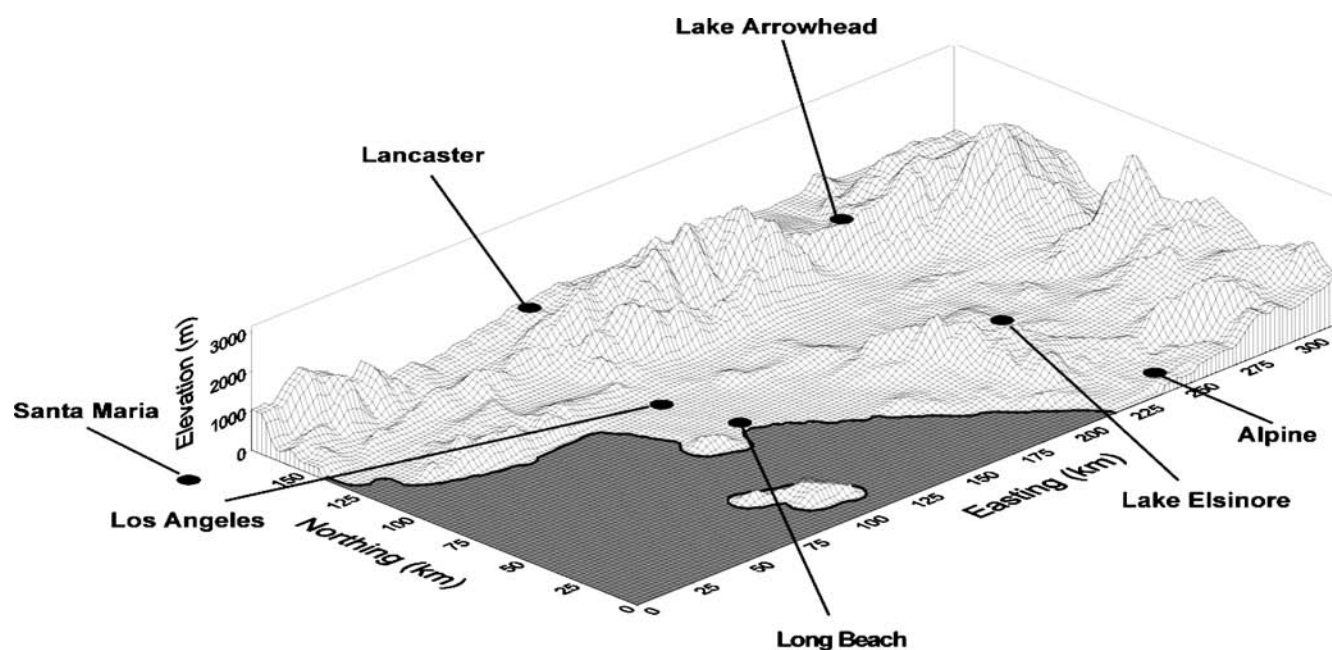

FIG. 1. Geographical location and elevation of the study sites. Santa Maria is located in central California; Los Angeles is shown only as a reference.

between two 400 mesh stainless steel screens. A 2″ PUF plug was placed behind the screen to hold the ensemble together. This arrangement allowed for faster sample extraction changing Soxhlet extraction for ultrasonication. Details of the cleaning procedure for the XAD-4, the QFFs, and the PUFs are reported elsewhere (Eiguren-Fernandez et al. 2004). All matrices were kept at $-20°C$ prior to and after sampling, and transport to and from the field was achieved using portable coolers containing frozen blue ice. Field blanks were taken and analyzed for quality control.

2.3. Chemical Analysis

QFFs and XAD-4 resin were extracted by ultrasonication for 28 minutes with 15 and 80 mL of a mixture of a methylene chloride:acetonitrile mixture (2:1 v/v), respectively. QFF extracts were filtered using a 0.45 μm nylon filter (Waters Inc, Clifton, NJ), and the extract volume reduced to ~5 mL under room conditions. One mL aliquots were used for PAH assays and the remainder was archived for additional analyses in a $-20°C$ freezer. The XAD-4 resin extract was filtered using a Millipore vacuum system (Millipore Corp., Bedford, MA), and the extract volume reduced to ~10 mL. Two aliquots of 1 mL were taken for PAH quantification. A 20 μL aliquot from the first was injected directly into the HPLC to quantify the more volatile PAHs (naphthalene to phenanthrene). The second 1mL aliquot was volume reduced to ~100 uL for the quantification of the less volatile PAHs (anthracene to indeno[*1,2,3-cd*]pyrene). The entire extraction process was performed using amber glass vials under yellow light conditions to avoid photodecomposition. Field blanks were extracted and analyzed for every ten samples. To evaluate if positive (adsorption) or negative (desorption) artifacts occurred during sampling with QFFs, back-up filters were used in the sampling matrix. No measurable amounts of PAHs were observed in the back-up filters, indicating that positive and negative artifacts were negligible. The absence of high molecular weight PAHs in the vapor-phase implied that no significant particle penetration through the QFF occurred during sampling. Details of the quantification procedure for the target PAHs using HPLC with selective fluorescence are described elsewhere (Eiguren-Fernandez and Miguel 2003). PAH concentrations were within the calibration range; the results were only reported when the signal to noise concentration ratios were at least 3. SRM 1649a (NIST) was used to determine the analytical procedure precision (4.2%) and PAH extraction recovery efficiency (92–97%).

3. RESULTS

3.1. Spatial Variation

Observed concentration averages and relative standard deviations (RSD) for the vapor- and particle-phase PAHs along with their physical properties are shown in Table 1. RSDs were calculated using all concentrations obtained for each PAH over the entire observation period at each site (n = 24). Overall, the highest average total (VP+PP) PAH concentration (152 ng m^{-3}) was observed in Long Beach, a heavily urbanized area with high heavy duty diesel (HHD) and light duty vehicle (LDV) traffic, as well as substantial diesel emissions from ships and associated operations at the seaports of Long Beach and Los Angeles. The lowest concentration (94.5 ng m^{-3}) was observed in Alpine, a rural location 40 miles east of San Diego, CA. The annual average concentrations reported in this study are relatively lower than those reported for six other communities in southern California (Eiguren-Fernandez et al. 2004), where, with the exception of the rural area of Lompoc (71.8 ng m^{-3}), the concentrations ranged between 258 ng m^{-3} and 607 ng m^{-3}. Volatile PAHs, including naphthalene (NAP), acenaphthene (ACE), fluorene (FLU), and phenanthrene (PHE), accounted for 99% of the total PAH mass in the vapor-phase for all sites. For these PAHs, the annual average concentrations ranged from 89 ng m^{-3} to 142 ng m^{-3}, 0.71 ng m^{-3} to 1.38 ng m^{-3}, 1.15 ng m^{-3} to 2.13 ng m^{-3}, and 1.33 ng m^{-3} to 3.55 ng m^{-3}, respectively.

Among the particle-phase PAHs measured, BGP concentrations, an indicator of LDV emissions (Marr et al. 1999; Miguel et al. 1998), ranged between 48.2 pg m^{-3} and 231 pg m^{-3}. Long Beach and Lancaster presented the highest concentrations of this compound, suggesting that both sites are highly impacted by light duty vehicular emissions. In California no significant emissions from coal burning are expected, but biomass burning during the winter period may contribute to BGP concentrations in cold sites such as Lancaster and Alpine. BAP concentrations ranged from 19.8 pg m^{-3} in Santa Maria to 111 pg m^{-3} in Long Beach. The average annual distributions for target PAHs observed in the vapor- and the particle-phase (PM$_{2.5}$) for the six sites are shown in Figure 2. The lower molecular mass PAHs (NAP to ANT) were found mostly in the vapor-phase; the semi-volatiles (FLT to CRY) showed a clear partitioning between both phases. The larger molecular mass PAHs (BBF to BGP) were found nearly exclusively in the particle phase. The lowest total PAH concentrations were observed in Santa Maria and Lake Arrowhead, followed by Alpine. The highest vapor-phase concentrations were observed in Long Beach, while Lancaster showed the highest concentrations of particle-phase PAHs. It is important to note that naphthalene, defined by the US EPA as a hazardous air pollutant, and listed in the 2002 State of California's Proposition 65 program as a substance known to cause cancer, constitutes about 95% of the measured PAH mass reported in this study.

3.2. Seasonal Variation

Previous studies have shown that the effect of season on PAH concentrations is more pronounced for particle-phase PAHs (Eiguren-Fernandez et al. 2004; Terzi and Samara 2004; Tsapakis and Stephanou 2005). A recent study demonstrated the strong influence of season on the atmospheric chemistry of semi-volatile (2- to 4-ring) PAHs at a source and a receptor site

TABLE 1
Annual average concentrations (± RSD) for vapor- and particle-phase (PM$_{2.5}$) PAHs observed from July 2002 to November 2003

PAH\Site	Code	MW	(log p_L^0): a	Santa Maria (SMA)	Long Beach (LBC)	Lancaster (LCR)	Lake Elsinore (LKE)	Lake Arrowhead (LAH)	Alpine (ALP)
				Vapor-phase (ng m^{-3})					
Naphthalene	NAP	128	−3.53	103 ± 135	142 ± 112	128 ± 88.1	133 ± 179	103 ± 70.9	89.5 ± 106
Acenaphthene	ACE	154	−4.84	0.98 ± 1.66	1.38 ± 1.09	1.27 ± 2.57	0.71 ± 0.47	1.35 ± 1.66	0.74 ± 0.36
Fluorene	FLU	166	−5.18	1.68 ± 3.12	2.13 ± 2.07	2.03 ± 4.05	1.44 ± 0.88	1.15 ± 1.72	1.20 ± 0.39
Phenanthrene	PHE	178	−6.18	1.45 ± 1.34	3.55 ± 2.57	1.97 ± 4.05	2.09 ± 1.49	1.33 ± 0.75	1.70 ± 0.70
Anthracene	ANT	178	−6.23	0.09 ± 0.06	0.27 ± 0.26	0.12 ± 0.13	0.11 ± 0.15	0.02 ± 0.02	0.12 ± 0.13
Fluoranthene	FLT	202	−7.24	0.29 ± 0.25	0.54 ± 0.24	0.19 ± 0.09	0.31 ± 0.24	0.11 ± 0.06	0.34 ± 0.16
Pyrene	PYR	202	−7.48	0.23 ± 0.21	0.68 ± 0.43	0.25 ± 0.20	0.31 ± 0.28	0.08 ± 0.05	0.30 ± 0.14
Benz[a]anthracene	BAA	228	−8.49	0.11 ± 0.13	0.04 ± 0.07	0.04 ± 0.02	0.08 ± 0.04	0.05 ± 0.04	0.11 ± 0.07
Chrysene	CRY	228	−8.64	0.02 ± 0.01	0.03 ± 0.02	0.03 ± 0.03	0.06 ± 0.06	0.02 ± 0.02	0.03 ± 0.02
Benzo[b]fluoranthene	BBF	252	−9.63	b	0.03 ± 0.01	0.03 ± 0.02	b	0.02 ± 0.01	b
Benzo[k]fluoranthene	BKF	252	−9.63	b	0.07 ± 0.02	0.04 ± 0.01	b	0.02 ± 0.02	0.02 ± 0.01
Benzo[a]pyrene	BAP	252	−10.0	b	b	b	b	b	b
Indeno[1,2,3-cd]pyrene	IND	276	−10.0	b	b	b	b	b	b
Dibenz[a,h]anthracene	DBA	278	−10.7	b	b	b	b	b	b
Benzo[ghi]perylene	BGP	276	−10.7	b	b	b	b	b	b
ΣPAH (VP)				108	151	134	138	107	94.1

Site	Code	Santa Maria (SMA)	Long Beach (LBC)	Lancaster (LCR)	Lake Elsinore (LKE)	Lake Arrowhead (LAH)	Alpine (ALP)
		Particle phase (Pg m^{-3})					
	NAP	146 ± 186	134 ± 20.4	386 ± 610	111 ± 71.4	707 ± 925	62.8 ± 73.5
	ACE	73.5 ± 64.8	134 ± 54.7	303 ± 414	64.8 ± 20.7	453 ± 487	78.0 ± 34.1
	FLU	4.87 ± 1.33	7.77 ± 2.54	25.3 ± 49.5	15.6 ± 26.7	46.9 ± 71.1	8.87 ± 3.70
	PHE	26.1 ± 50.1	20.2 ± 16.5	52.9 ± 84.5	35.3 ± 36.0	74.5 ± 112	32.9 ± 25.3
	ANT	1.94 ± 1.37	4.81 ± 4.40	6.22 ± 10.9	4.04 ± 3.80	8.00 ± 11.9	3.36 ± 2.57
	FLT	17.0 ± 21.0	32.2 ± 33.3	44.8 ± 70.1	36.6 ± 51.1	42.9 ± 79.8	22.3 ± 21.4
	PYR	12.2 ± 10.4	43.2 ± 55.2	77.2 ± 169	31.7 ± 26.1	48.3 ± 100	22.0 ± 17.3
	BAA	10.4 ± 11.1	34.5 ± 39.5	96.3 ± g183	18.5 ± 23.6	72.4 ± 110	14.3 ± 11.8
	CRY	20.7 ± 19.9	53.8 ± 78.5	99.5 ± 207	32.3 ± 44.6	35.4 ± 62.2	26.9 ± 23.0
	BBF	27.8 ± 23.7	78.9 ± 128	117 ± 203	46.0 ± 62.9	37.0 ± 63.4	32.1 ± 25.3
	BKF	12.9 ± 12.6	43.6 ± 76.6	77.3 ± 143	19.0 ± 25.1	12.2 ± 18.1	14.7 ± 12.9
	BAP	19.8 ± 23.4	74.9 ± 147.7	111 ± 216	32.7 ± 53.1	32.0 ± 67.8	22.3 ± 25.6
	IND	31.8 ± 36.2	102 ± 170.5	153 ± 239	36.7 ± 58.3	33.0 ± 73.1	28.4 ± 25.1
	DBA	3.03 ± 3.76	15.4 ± 36.0	43.3 ± 125	4.14 ± 7.65	4.33 ± 8.01	2.50 ± 2.28
	BGP	64.9 ± 52.0	231 ± 370	182 ± 284	69.0 ± 87.7	48.2 ± 90.0	50.3 ± 39.1
ΣPAH (PP)		473	1010	1775	557	1655	422
ΣPAH (VP+PP), ng m^{-3}		108	152	136	139	109	94.5

a: sub-cooled liquid vapor pressure (atm at 25 °C) Calvert et al. 2002; b: below limit of detection
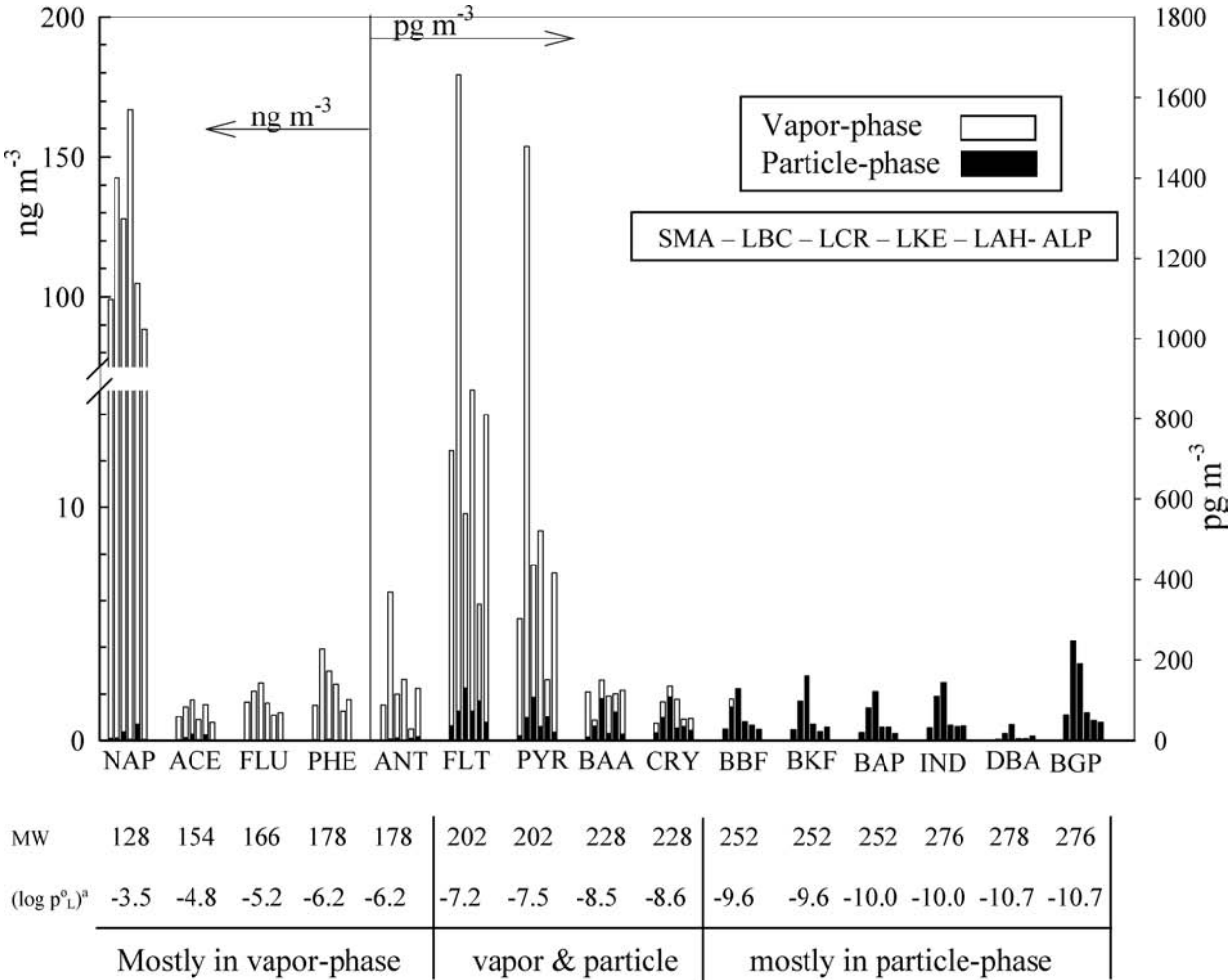
FIG. 2. Vapor- and particle-phase annual distribution of the target PAHs and their corresponding sub-cooled liquid vapor pressure (atm). a: sub-cooled liquid vapor pressure (atm at 25°C) Calvert et al. 2002.

in the Los Angeles basin (Reisen and Arey 2005). To analyze the effects of ambient temperature on the observed PAH concentrations, although the changes on temperature in Southern California are not dramatic, we separated the concentration data into three sub-groups based on the average temperature over the sampling season. Seasonal average concentrations observed in Long Beach and Lancaster for vapor-phase, semi-volatile, and particle-phase PAHs are shown in Figures 3a–c. Similar results were obtained for all six sites. Observed seasonal variation in VP-PAHs was not dramatic, although slightly higher concentrations are observed during the "cold" season; warm season VP PAH concentrations were lower for all sites (Figure 3a). For the semi-volatile group, from FLT to CRY, as exemplified for Long Beach and Lancaster, observed concentrations show a trend towards increasing concentrations as temperature decreases towards the cold season (Figure 3b). As these PAHs are found both in the vapor- and the particle-phase, partitioning from the vapor- to the particle-phase would be favored as the temperature of the season decreases. Dramatic increases in particle-phase

PAHs (BBF to BGP) concentrations are observed from hot to cold season (Figure 3c). For these species, hot season concentrations varied from 0.3 to 34 pg m^{-3}, the warm season ranged from 1.69 to 75 pg m^{-3}, and cold season from 5.73 pg m^{-3} to 654 pg m^{-3}. Cold/hot season concentration ratios calculated for the respective particle-phase PAHs are shown in Figure 4. The average ratio for all sites was 5.7, with a 54 maximum observed in Long Beach for DBA. Among the six communities, the strongest effect of seasonal changes, as indicated by the cold to hot season ratio (Figure 4) is observed in Long Beach, an area with a large amount of light- and heavy duty-vehicle traffic and ship emissions, and in Lancaster, a high desert dormitory community with high commuter traffic. The differences in seasonal characteristics may also be caused by different source activity. For instance, wood combustion tends to occur mainly in the winter season. Although many different PAH species are found in wood smoke, Fine et al. (2004) reported that, other than retene, pyrene, fluoranthene, and coronene were among the most prevalent wood smoke PAHs. If this were the case, the cold/hot ratios

a) Vapor-phase
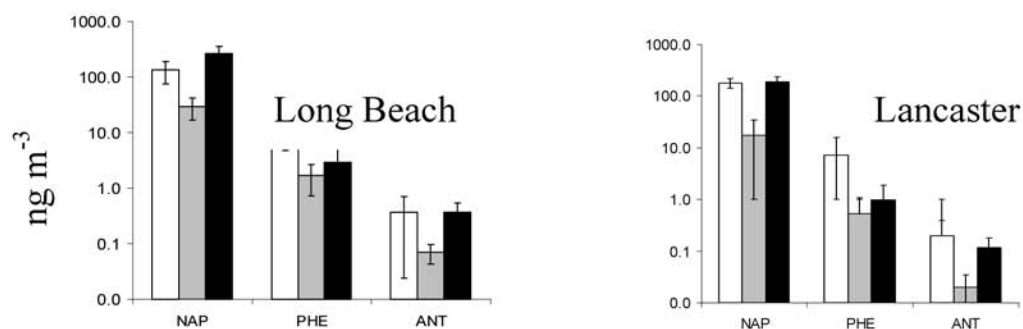
b) Semi-volatile
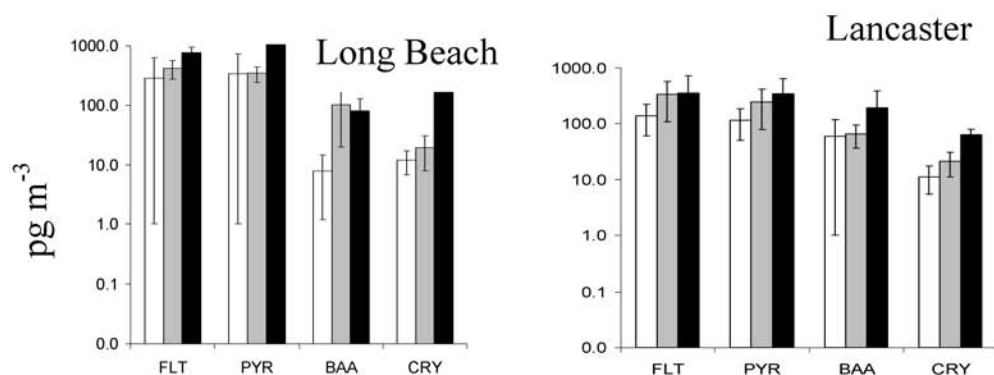
c) Particle-phase
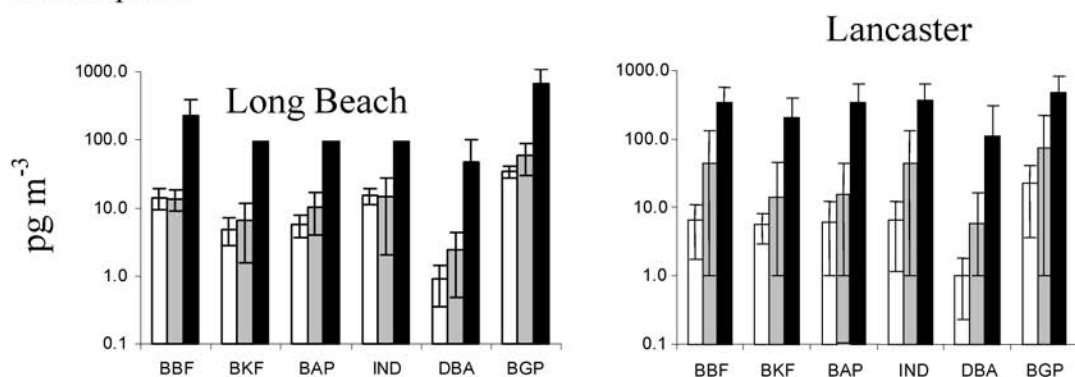
Long Beach: ☐ Hot season (25.1°C)　☐ Warm season (24.7°C)　■ Cold season (19.6° C)

Lancaster:　☐ Hot season (30.4°C)　☐ Warm season (29.4°C)　■ Cold season (12.2°C)

FIG. 3.　Seasonal average concentrations and ranges observed for selected PAHs. Temperatures represent seasonal averages based on 24-hr measurement periods measured at each site. (a) Vapor-phase; (b) Semivolatile; (c) Particle-phase.

☐ SMA   ■ LBC   ◨ LCR   ▩ LKE   ▤ LAH   ☐ ALP

Half-life* >70 d 190 min >400 d 5.7 d 34 d 24 d >300 d >300 d 200 min >800 d 29 d 5.5 d
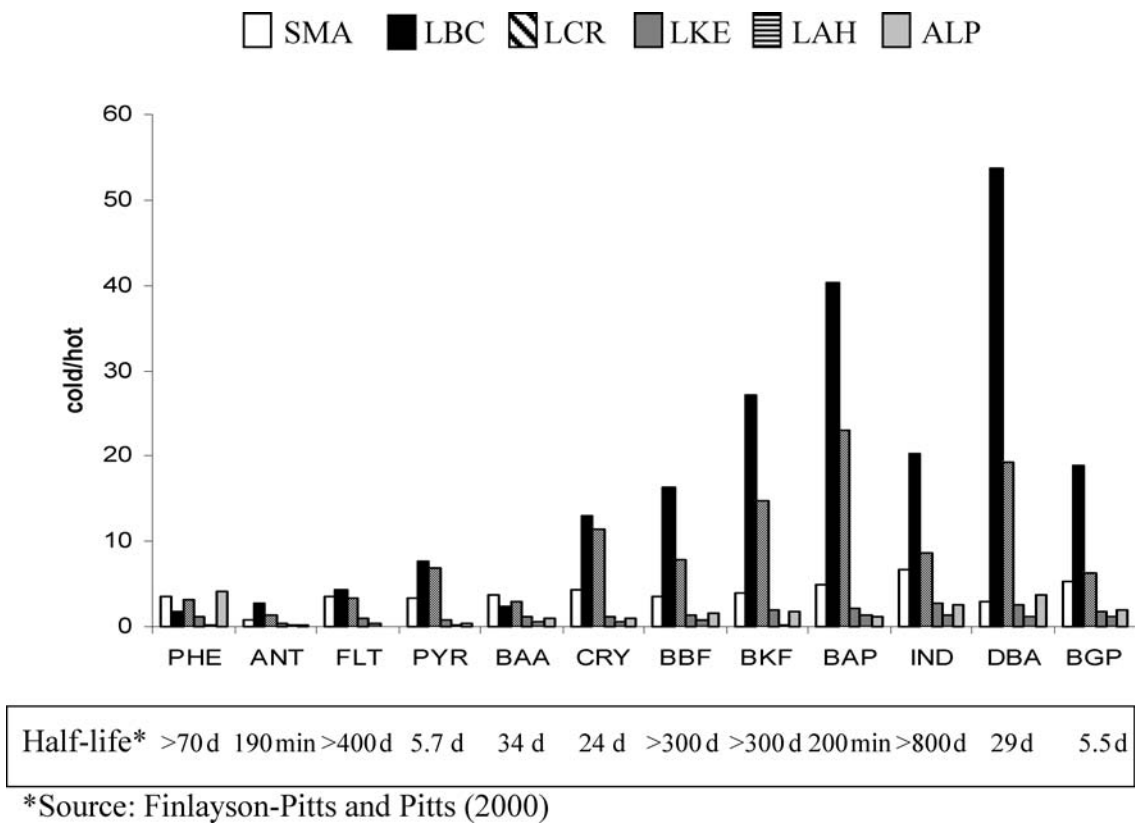
*Source: Finlayson-Pitts and Pitts (2000)

FIG. 4.   Seasonal cold/hot concentration ratios for particle-phase PAHs at all sites.

for pyrene and fluoranthene shown in Figure 4 should present the largest seasonal variation. Thus, the present study results suggest that winter wood combustion contribution to the measured PAHs is not prevalent.

The PAH half-lives, the cold/hot concentration ratios (Figure 4), and the seasonal averages observed for the particle-phase species (Figure 3c) provide an indication of the important role of meteorology, as compared with photochemistry, in determining the concentration of particle-phase PAHs at each study site. If atmospheric reactivity were the dominating factor, we should expect that species found mainly in the particle-phase with short life-times due to photochemical reactions (e.g., 200 min for BAP, 190 min for ANT (Finlayson-Pitts and Pitts 2000)) would have much a higher cold/hot season ratios. This is clearly not the case. The observation that several particle-phase PAHs with longer life-times—ranging from 5.5 days to >300 days—(Finlayson-Pitts and Pitts 2001) had higher cold/hot season ratios suggests that meteorology, expressed as lower temperatures, lower surface and boundary mixing layers, and weaker advective atmospheric mixing, constitute a dominant mechanism determining PAH concentrations, and thus human exposure. These observations are relevant to future interpretation and analysis of community-scale human health effects research.

3.3.   Highlights and comparison with previous measurements

In our previous study (Eiguren-Fernandez et al. 2004), ambient PAH concentrations were measured over a one year sampling period in four urban communities located 40–100 km downwind of the city of Los Angeles, and two rural upwind sites. In the current study, with the exception of the Long Beach site, which is highly impacted by port activity emissions (ships, heavy-duty diesel trucks, automobiles, and trains), samples were collected in rural communities that are less affected by atmospheric transport. In the current study, at all six sites, PAH levels are in general 2–3 times lower than those found in our previous study, especially for naphthalene, the most volatile PAH. Average PAH concentrations are more similar among the rural sites suggesting that local traffic and cooking emissions may be the major contributors to the PAH burden. For all twelve sites in the current and the previous study, naphthalene was the dominant PAH, accounting for up to 99% of the total mass. Because naphthalene is ubiquitous in the Southern California air, it should be the subject of continued toxicological and epidemiological studies. Season and ambient temperature showed again to have a significant effect on PAH levels, which increased with colder temperatures. At the rural higher altitudes sites, lower cold/hot ratios were observed. Long Beach and Lancaster (a more populated area

than that of the other sites) were the only sites showing ratios comparable to the previous results. The fact that differences in PAH levels from hot to cold seasons are less significant at the rural sites further suggest that local emissions are more important than atmospheric transport.

4. CONCLUSIONS

Vapor-phase PAHs dominate the atmospheric PAH loading with naphthalene representing the major contributor. Vapor-phase concentrations did not vary significantly over the course of a year, reflecting their inherently low vapor/particle partition coefficient. A significant seasonal variation was observed for particle-phase PAHs (BBF to BGP), suggesting that meteorological conditions rather than reactivity constitute the dominant factor. Understanding the vapor- and particle-phase partitioning of atmospheric PAHs and their seasonal and spatial variations is very important for risk assessment studies. Given the very high concentrations of naphthalene observed in Southern California, and its recent inclusion in the carcinogen list of the State of California, we recommend that this PAH be included in all future PAH exposure assessments. In addition, because particle-phase PAH loadings increase significantly as temperature decreases, epidemiological analyses should always consider seasonal variations as one of the variables when evaluating the role of PM chemical content on particle toxicity.

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